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Efficient Implementation of the Gauge-Independent Atomic Orbital Method for NMR Chemical Shift Calculations

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Abstract: An implementation of the gauge independent atomic orbital (GIAO) method for the ab initio self-consistent-field (SCF) calculation of nuclear magnetic resonance (NMR) chemical shifts is described. Using modern techniques borrowed from analytical derivative methods, we were able to improve the efficiency of the GIAO method significantly. Results with several basis sets, some of them large, are presented for methane, methyl fluoride, cyclopropene, cyclopropane, oxirane, benzene, carbon disulfide, the sulfate and thiosulfate anions, dimethyl sulfide, dimethyl sulfoxide, and dimethyl sulfone. Computer timings for energy and chemical shielding calculations are given for a few large organic molecules. Comparisons are made with the individual gauge for localized orbitals (IGLO) method of Schindler and Kutzelnigg, and with the localized orbital/local origin (LORG) method of Hansen and Bouman. The GIAO method appears to converge faster than the localized techniques; i.e., it provides the same accuracy with a smaller basis, particularly for the individual tensor components. The computational effort for the ab initio calculation of the NMR chemical shifts is only ~2.5 times of the energy calculation.

I. Introduction

Modern high-field, multipulse NMR spectroscopy has proven to be an exceptionally powerful technique for solution of many types of problems in chemistry and biochemistry. However, the problem of correct signal assignment as well as the understanding of the relationship between the chemical shift and molecular structure can be quite difficult. Ab initio calculations are now becoming affordable and accurate enough to be useful in the solution of some of these problems. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic chemical shift-molecular structure relationship.

Calculations of magnetic shielding tensors have been performed at various theoretical levels. Semiempirical methods[1] provide a correct qualitative understanding but are not accurate quantitatively. Almost all ab initio results are at the SCF level, and are thus based on the coupled Hartree-Fock perturbation theory (CHF).[2] A common difficulty in the calculation of magnetic properties is that the usual wave functions do not guarantee gauge invariance;[3] i.e., in the simplest case, the results may depend on the position of the molecule in the Cartesian frame. The physical reason for this is that a magnetic field, say in the z direction, leads to a perturbation *in the momenta*, which twists the molecular orbitals around the z axis in the imaginary xy plane. If an atom is situated on the z axis, its basis set is closed under this rotation, and it can be described equally well both unperturbed and in the presence of the perturbation. However, for an atom far from the z axis, the rotation of the orbitals can only be described by using high angular momentum basis functions, which are not normally included in the basis.

There are two general approaches to solve the gauge problem. Very large basis sets lead to approximate gauge invariance since in the limit of complete basis sets the results should be gauge independent.[4] A number of calculations have been published by this method for small molecules.[2,5] In our opinion, however, this is not a viable technique for larger systems. The second approach introduces local gauge origins to define the vector potential of the external magnetic field. This idea was first suggested and used by London in the study of molecular diamagnetism over 50 years ago.[6] For magnetic shielding calculations, it was first adapted by Ditchfield in the gauge invariant atomic orbitals (GIAO) method.[7] In Ditchfield's method each atomic orbital has its own local gauge origin placed on its center. Following Ditchfield's work, the GIAO method has been also implemented by Giessner-Prettre et al.[8] and by Fukui et al.[9] The GIAO method has been successfully used in calculations for small- and medium-size systems.[10]

In spite of these successes, it appears that the existing implementations of the GIAO method require too much in computing resources to be routinely applicable to large molecules. Chesnut et al.[11] have recently suggested a way to improve the efficiency of GIAO calculations by using "attenuated" basis sets, which describe well the nuclei under consideration and less accurately the others. In our opinion this method may be inefficient when chemical shifts for a number of nuclei are needed, e.g., in $C_{16}H_{24}$ discussed later in this paper. Other, more promising methods improve the efficiency of the GIAO calculations by applying the gauge factors to localized molecular orbitals instead of every atomic orbital. Two such methods have been developed recently: the individual gauge localized orbital (IGLO) method by Schindler and Kutzelnigg[12] and the localized orbital/local origin (LORG) method by Hansen and Bouman.[13] In practice, both methods

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have been remarkably successful. However, they may encounter difficulties in molecules with delocalized electron structure and, consequently, strong ring currents. Moreover, like all methods based on localized MOs, the results are slightly ambiguous when there is no unique localization. One of the purposes of the present paper is to compare a modern GIAO implementation with the IGLO and LORG methods.

In spite of the good performance of the methods based on localized orbitals, an efficient implementation of the GIAO method would be, in our opinion, preferable for the following reasons:

(i) Compared with the GIAO method, the localized methods introduce a further approximation in the form of the closure relation, which holds only for complete basis sets.

(ii) The wave function is more flexible in the GIAO method than in the localized ones. Both (i) and (ii) would lead to the expectation that the localized methods are more sensitive to the quality of the basis set than the GIAO technique.

(iii) The localized theories are not expected to perform well for systems with inherently delocalized orbitals. The electronic structure of most simple organic molecules (even that of conjugated polyenes) is well localizable. Nevertheless, a number of electron-deficient compounds, inorganic compounds, and unusual structures exist where localizability is questionable or poor.

(iv) Finally, generalization of the GIAO formalism to correlated wave functions is straightforward. Such generalization appears to be more difficult for the localized theories.

II. Theory

Below we recapitulate the theory of magnetic shielding[6,7,14] in order to establish the notation. The magnetic shielding constant, $\mathbf{B}_n$, is the second derivative of the molecular energy with respect to the external magnetic field, **H**, and the nuclear magnetic moment of a given nucleus n. This second-order quantity is represented by a nonsymmetric tensor with nine independent components. In the coupled Hartree–Fock theory, using atomic orbital throughout, the tensor component *ab* ($a, b = x, y, z$) for nucleus n is given by

$$B_n^{ab} = \mathrm{Tr}\{\mathbf{D}^{oo} \times \mathbf{h}_n^{ab}\} + \mathrm{Tr}\{\mathbf{D}^{ao} \times \mathbf{h}_n^{ob}\} \qquad (1)$$

where **D** is the first-order reduced density matrix, and **h** is the matrix of the one-electron part of the Hamiltonian. The superscripts represent differentiation with respect to the external magnetic field, and the nuclear magnetic moment, in this order. The first term in eq 1 is the diamagnetic component of the shielding and the second term represents the paramagnetic part; the latter depends on the first-order density matrix $\mathbf{D}^{ao}$. The formulas for the derivative matrix elements $\mathbf{h}_n^{11}$ depend on the type of basis set employed: fixed or field dependent. In the GIAO method with explicitly field-dependent basis functions

$$\chi_p(\mathbf{H}) = \exp[(-i/2c)(\mathbf{H} \times \mathbf{R}_p)\cdot \mathrm{r}]\chi_p(0) \qquad (2)$$

these are the derivatives of the matrix elements of the bare nucleus Hamiltonian **h**:

$$(\mathbf{h}_n^{ab})_{pq} = \langle p^a|h_n^{ob}|q\rangle + \langle p|h_n^{ob}|q^a\rangle + \langle p|h_n^{ab}|q\rangle \qquad (3)$$

where p^a denotes first derivative of the basis function, eq 2, with respect to the *a* component of the magnetic field. The derivative one-electron operators in the above equations are given as

$$h_n^{ab} = (1/2c^2)[\mathrm{r}\cdot(\mathrm{r} - \mathbf{R}) - \mathrm{r}_a\,(\mathrm{r} - \mathbf{R})_b]/|\mathrm{r} - \mathbf{R}|^3 \qquad (4)$$

$$h_n^{ob} = (-i/c)[(\mathrm{r} - \mathbf{R}) \times \nabla]_b/|\mathrm{r} - \mathbf{R}|^3 \qquad (5)$$

where r is the electron position vector, **R** is the position vector of nucleus n, *c* is the speed of light, and the symbols for dot and cross products have their usual significance.

The first-order density matrices needed for paramagnetic shielding are solutions of the appropriate CHF equations with the external magnetic field as a perturbation.[3,7] While the original derivation of the GIAO CHF[7] method uses the SCF orbitals explicitly, we found it convenient to formulate it in terms of the Fock–Dirac density matrix,[15] which is invariant with respect to unitary transformation of the orbitals. In this formalism with a nonorthogonal and field-dependent basis set, the CHF perturbation equations can be written in matrix form as

$$\mathbf{F}^1\mathbf{D}^0\mathbf{S}^0 + \mathbf{F}^0\mathbf{D}^1\mathbf{S}^0 + \mathbf{F}^0\mathbf{D}^0\mathbf{S}^1 = \mathbf{S}^1\mathbf{D}^0\mathbf{F}^0 + \mathbf{S}^0\mathbf{D}^1\mathbf{F}^0 + \mathbf{S}^0\mathbf{D}^0\mathbf{F}^1 \qquad (6)$$

$$\mathbf{D}^1\mathbf{S}^0\mathbf{D}^0 + \mathbf{D}^0\mathbf{S}^1\mathbf{D}^0 + \mathbf{D}^0\mathbf{S}^0\mathbf{D}^1 = 2\mathbf{D}^1 \qquad (7)$$

Equation 7 arises from orthonormality constraints, while eq 6 represents the Hartree–Fock equations in first-order perturbation theory. In eq 6, and in the following, we do not explicitly denote the Cartesian components, only the order of the perturbation due to the external magnetic field. **F**, **D**, and **S** are the Fock, density, and overlap matrices, respectively. Symbols without superscript denote zeroth-order (unperturbed) quantities. The first-order Fock matrix is given by

$$\mathbf{F}^1 = \mathbf{h}^1 + \mathbf{G}(\mathbf{D}^1,g^0) + \mathbf{G}(\mathbf{D}^0,g^1) \qquad (8)$$

where

$$\mathbf{G}(\mathbf{D}^1,g^0)_{pq} = \textstyle\sum_{rs} D^1{}_{rs}\,g^0{}_{pq,rs}$$

$$\mathbf{G}(\mathbf{D}^0,g^1)_{pq} = \textstyle\sum_{rs} D^0{}_{rs}\,g^1{}_{pq,rs}$$

and

$$\mathbf{h}^1{}_{pq} = \langle p^1|\mathbf{h}|q\rangle + \langle p|\mathbf{h}^1|q\rangle + \langle p|\mathbf{h}|q^1\rangle$$

The first derivative of the bare nucleus Hamiltonian with respect to the external magnetic field is $\mathbf{h}^1 = (-i/2c)\mathrm{r} \times \nabla$. The two-electron integrals are denoted by $g_{pqrs} = g^0{}_{pqrs} = (pq|rs) - 0.5(ps|rq)$; their first derivatives are g^1. The solution of the CHF eq 6 provides the first-order density matrices $\mathbf{D}^a$, $a = x, y, z$. Equation 6 can be conveniently rewritten as

$$\mathbf{D}^1 = 0.5 \times \mathbf{D}^0\mathbf{S}^1\mathbf{D}^0 + \textstyle\sum_{ia}(e_i - e_a)^{-1} \times \mathbf{C}_i^{\dagger}(\mathbf{F}^1 - e_i\mathbf{S}^1)\mathbf{C}_a \times (\mathbf{C}_i\mathbf{C}_a^{\dagger} - \mathbf{C}_a\mathbf{C}_i^{\dagger}) \qquad (9)$$

where $\mathbf{C}_i$ and $\mathbf{C}_a$ denote column vectors of the unperturbed occupied and virtual orbitals, respectively, and the corresponding orbital energies are e_i and e_a. Equation 9 must be solved iteratively because $\mathbf{F}^1$ depends on $\mathbf{D}^1$.

III. Efficiency of the GIAO Method

The amount of computer time and memory required by GIAO programs was a major obstacle for the routine application of this method for NMR chemical shift calculations. In the past 20 years, much effort has been spent on improving the efficiency of ab initio analytical derivative theory. It was pointed out recently[16] that these advances can be used to improve significantly the efficiency of NMR chemical shift calculations. Although the physical perturbation caused by changing the nuclear coordinates and by applying an external magnetic field is very different, mathematically they have much in common. In both cases, the most time-consuming part of the calculation arises from perturbations in the basis sets. As pointed out above, a uniform magnetic field in the *z* direction rotates the GIAO functions, eq 2, in the imaginary *xy* plane around the *z* axis. A compelling analogy with the gradient method is obtained by absorbing the gauge factor in the center coordinates of Gaussians, which now move in the complex space by an amount proportional to the external magnetic field.[16] The possibility of representing gauge factors by single Gaussians with complex coordinates was first pointed out by Hall.[17] The presence of imaginary quantities, instead of the real per-

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Table I. Convergence of the Calculated NMR Shielding with the Basis Set in the GIAO Method for Methane and Methyl Fluoride (ppm)

Methane

basis set	energy, au	isotropic shielding	
		^{13}C	^{1}H
6-31G	−40.180513	207.36	32.93
6-31G (d, p)	−40.201662	202.62	31.75
6-311G	−40.188113	203.59	32.83
6-311G (d, p)	−40.209003	197.09	31.88
6-311G+(d,p)	−40.209080	196.97	31.87
6-2111G+(d,p)	−40.210176	194.73	31.62
6-311G+(2d,2p)	−40.212095	196.33	31.67

Methyl Fluoride[a]

basis set	^{13}C shielding			^{19}F shielding		
	iso	par	perp	iso	par	perp
6-31G	142.28	198.94	113.95	489.35	439.93	514.06
6-31G (d,p)	137.00	192.69	109.15	485.48	438.71	508.86
6-311G	136.82	194.61	107.93	487.18	437.71	511.92
6−311G (d,p)	128.36	186.95	99.08	483.06	437.59	505.79
6-311G+(d,p)	127.39	187.53	97.32	484.44	438.95	507.18
6-311G+(2d,2p)	126.23	187.09	95.79	483.34	438.88	505.57

[a] par and perp denote the component of the shielding parallel and perpendicular to the C_3 axis; iso is the isotropic average. In the calculations with diffuse functions, the latter were placed only on heavy atoms.

Table II. Comparison of the IGLO,[a] LORG,[a] and GIAO Results for ^{13}C and ^{19}F Absolute Shieldings and Anisotropies in CH_3F and CH_4

method, basis set	CH_3F				CH_4
	^{13}C shielding		^{19}F shielding		
	iso	aniso	iso	aniso	
IGLO[b]					
A	164	72	465	+26	219
B	158	81	542	+7	222
C	147		488		215
D	124	90	450		195
II	127	87	446	−60	
III	122	92	474	−66	
LORG					
4-31G	165	77	403	+30	221
4-31G (d)	148		450		212
4-31G (d,p)	145		450		207
6-311G (d,p)	132	85	454		197
GIAO					
4-31G	142	85	489	−75	206
4-31G (d)	135	82	484	−71	200
4-31G (d,p)	137	83	484	−69	201
6-311G (d,p)	128	88	483	−68	197
6-311G+(d,p)	127	90	484	−68	197
6-311G+(2d,2p)	126	91	483	−67	196
exptl[c]	132		471		197
exptl[d]	116.8	90	471	−90 ± 4	

[a] IGLO (A−D) and LORG results from ref 35, IGLO (II and III) results from ref 36. The anisotropy is $\sigma_{zz} - \sigma_{xx}$ where z is the symmetry axis. [b] Huzinaga's basis sets: A, C.F(73/42), H(3/2). B, C,F(95/42), H(3/2). C, C,F(951/531), H(51/31). D, C,F(1172/762), H(72/62). II, C,F(951/541), H(51/31). III, C,F(1172/762), H(62/42). [c] Reference 35. [d] Chestnut, D. B.; Phung, C. G. *J. Chem. Phys.* **1989**, *91*, 6238.

Table III. Convergence of the Calculated Isotropic NMR Shielding with the Basis Set in the GIAO Method for Three-Membered Rings

Cyclopropene

basis set	energy, au	isotropic shielding		
		$^{13}CH_2$	$^{13}C=$	$^{1}H^{a}$
6-31G	−115.765846	209.56	88.30	32.07
6-31G (d,p)	−115.829123	201.20	89.24	31.17
6-311G	−115.788724	203.59	73.88	31.77
6-311G (d,p) p)	−115.850880	195.10	73.62	31.19
6-311G+(d,p)	−115.852080	194.98	73.32	31.08
6-311G+(2d,2p)	−115.857193	193.99	73.08	30.89

Cyclopropane

basis set	energy, au	isotropic shielding	
		^{13}C	$^{1}H^{a}$
6-31G	−117.007492	208.98	33.08
6-31G (d,p)	−117.068328	203.45	31.90
6-311G	−117.029754	204.09	32.99
6-311G (d,p)	−117.087969	197.97	32.07
6-311G+(d,p)	−117.088500	197.84	32.04
6-311G+(2d,2p)	−117.093995	197.09	31.84

Ethylene Oxide

basis set	energy, au	isotropic shielding		$^{1}H^{a}$
		^{17}O	^{13}C	
6-31G	−152.783107	375.08	172.26	30.94
6-31G (d,p)	−152.871980	377.0	165.76	29.77
6-311G	−152.823643	373.75	167.15	30.86
6-311G (d,p)	−152.905999	375.76	158.74	29.89
6-311G+(d,p)	−152.909907	375.67	157.70	29.88
6-311G+(2d,2p)	−152.916178	375.36	156.41	29.65

[a] ^{1}H shieldings for the hydrogen in the methylene groups.

turbation caused by moving the nuclei in gradient theory, is only a minor complication.

The following techniques have been used to implement an efficient ab initio GIAO chemical shift program:

(1) Calculation of the perturbed two-electron integral by the quadrature technique of Dupuis, Rys, and King.[18] This is one of the modern methods for integral evaluation, although competing methods,[19] in particular the Obara–Saika recursive method as implemented by the Pople group,[20] have lower operation counts than the original Rys polynomial method. However, the latest implementations of the Rys polynomial method are much more efficient than the original one and they vectorize excellently on vector computers.[21] For this reason, we chose the Rys method.[18] However, we are currently exploring the use of the Obara–Saika-type methods. No complications arise from the presence of imaginary terms.

(2) Elimination of the storage for perturbed two-electron integrals. This step is a bottleneck in existing implementations of the GIAO method[8] as well as in the first implementations of analytical force constant calculation. The bottleneck is eliminated by storing only the three contributions to the derivative Fock matrices, $G(D^0, g^1)$ in eq 8, instead of the integrals.[22]

(3) Formulation of the coupled-perturbed Hartree–Fock equations fully in atomic orbital (AO) basis, thus avoiding the four-index transformation of the integrals that is present in other implementations.[9] These equations have traditionally been formulated in a molecular orbital (MO), or mixed MO–AO basis.[23] The full AO formulation was recommended by Pulay[22] and Osamura et al.[24] For analytical force cosntant calculations, the AO method may not be more advantageous than the MO one, particularly on vector computers, because a large number of CHF

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Table IV. ^{13}C NMR Shift Tensors in the Methylene Groups of Three-Membered-Ring Compounds Relative to Methane (ppm)[a]

			principal components[c]		
method	iso	aniso	AA	BB	CC
	Cyclopropene				
IGLO (DZ)	4	89	54	13	−55
LORG (TZP)	−2	107			−73[b]
GIAO					
6-31G	−2	105	43	22	−72
6-31G (d,p)	1	103	42	30	−67
6-311G	0	108	44	28	−72
6-311G (d,p)	2	109	43	34	−71
6-311G+(d,p)	2	109	43	34	−71
6-311G+(2d,2p)	2	108	43	34	−70
exptl	3	94	40	29	−59
	Cyclopropane				
IGLO (DZ)	10	31	42	−1	−10
III (TZP)	−3	55.5	25	6	−40
IV (QZP)	−1.3	58	27	9	−40
LORG (TZP)	0	53			−35[b]
GIAO					
6-31G	−2	49	26	4	−35
6-31G (d,p)	−1	52	25	7	−35
6-311G	−1	53	27	8	−36
6-311G (d,p)	−1	56	26	10	−38
6-311G+(d,p)	−1	57	26	10	−38
6-311G+(2d,2p)	−1	56	26	10	−38
exptl	−4	48	22	2	−36
	Ethylene Oxide				
IGLO (DZ)	31	34	74	10	8
III (TZP)	39.3				
V (QZ2P)	45	48	92	29	13
LORG (TZP)	38	45			8[b]
GIAO					
6-31G	35	43	79	20	6
6-31G (d,p)	37	45	81	23	7
6-311G	36	45	80	22	7
6-311G (d,p)	38	47	84	24	7
6-311G+(d,p)	39	46	85	24	9
6-311G+(2d,2p)	40	45	86	24	10
exptl	44	37	93	19	19 (??)

[b] Calculated from isotropic and anisotropy shift. [c] AA is the CCC or COC bisector, BB is in the CCC or COC plane, and CC is out of plane.

equations must be solved. Once the transformation has been made the solution is significantly faster in MO basis (see, e.g., ref 16). This argument does not apply, however to the present case where there are only three equations.

(4) Solution of the CHF perturbation eq 9 by a conjugate gradient type method.[25] This is a modification of the convergence acceleration introduced by Pople et al.[26] for the solution of the CHF equations. Subsequently, it was pointed out by Wormer et al.[27] that this method is equivalent to the conjugate gradient technique and can make use of a three-term recursion formula. The advantage of using the conjugate gradient formulation is reduced storage requirement (only three densities and the corresponding residuals need to be stored) and simpler program organization (the matrix dimensions do n ow as the iteration progresses). In spite of its clear advantages, the method of Wormer et al.[27] has not become widely recognized. The convergence rate of the modified method is identical with the original one; convergence to an accuracy of 10^{-6} in the first-order density matrix is usually achieved in 10 or fewer iterations. All three (x, y, z) CHF equations are solved simultaneously.

(5) Screening of the perturbed two-electron integrals and the calculation of only those that contribute significantly to the magnetic shieldings. The contributions of the two-electron integral

Table V. Calculated NMR Shielding and Chemical Shift Tensors for Benzene

(a) Convergence of the Calculated NMR Shielding with the Basis Sets in the GIAO Method for Benzene (ppm)

		isotopic shielding	
basis set	energy, au	^{13}C	^{1}H
6-31G	−230.623649	74.20	25.54
6-31G (d,p)	−230.712713	73.27	24.49
DZ (9s5p/4s)	−230.641136	66.17	25.14
6-311G	−230.661957	62.70	25.53
6-311G (d,p)	−230.753119	58.67	24.57
6-311G+(d,p)	−230.755905	58.54	24.54
6-311G+(2d,2p)	−230.766561	57.73	24.20
exptl gas[a]		57.2	

(b) Chemical Shift Tensors in Benzene Relative to CH_4 (ppm)[b]

	^{13}C					^{1}H	
			principal components				
method	iso	aniso	AA	BB	CC	iso	aniso
IGLO (DZ)	131	211				8.69	−5.1
LORG (DZ)	135	197	260	141	4		
CHF	140	201	252	162	6		
GIAO:							
6-31G	133	193	247	147	5	7.39	−4.13
6-31G (d,p)	129	184	240	141	7	7.26	−5.53
6-311G	141	199	263	151	8	7.30	−3.95
6-311G (d,p)	138	194	259	148	9	7.31	−5.33
6-311G+(d,p)	139	196	260	147	8	7.23	−5.02
6-311G+(2d,2p)	139	195	260	148	8	7.47	−5.35
exptl (gas)	137.2						
exptl (solid)	132	181	236	148	11	7.24	−3.9

[a] Reference 38. [b] IGLO results from ref 12c; LORG, CHF, and experimental results from ref 13, except for the gas-phase data.[38] The AA direction is in the CCC plane parallel to the C–H bond, BB is in the CCC plane perpendicular to the C–H bond, and CC is out of plane.

derivatives are estimated by the uncoupled Hartree–Fock procedure.[28] In this approximation the terms containing the first-order density matrix, $\mathbf{D}^1$, are neglected in eq 8, resulting in a noniterative formula for the first-order density. It is now accepted that the uncoupled Hartree–Fock theory[28] usually overestimates second-order properties and may be in error by a factor of 2 or 3. We believe, however, that it is accurate enough to estimate the order of magnitude of the contributions. A convenient property of the present formulation is that the estimated contributions to the chemical shielding can be written in a simple *effective density matrix* form. In the uncoupled approximation, the two-electron part of the first-order density matrix in the external magnetic field, $\mathbf{P}^1$, is given by

$$\mathbf{P}^1 = \textstyle\sum_{\mathrm{i,a}}(e_\mathrm{i} - e_\mathrm{a})^{-1} \times \mathbf{C}_\mathrm{i}^\dagger \mathbf{G}(\mathbf{D},g^1)\mathbf{C}_\mathrm{a} \times (\mathbf{C}_\mathrm{i}\mathbf{C}_\mathrm{a}^\dagger - \mathbf{C}_\mathrm{a}\mathbf{C}_\mathrm{i}^\dagger) \qquad (10)$$

Substituting this into the formula for the paramagnetic part of the chemical shielding

$$\sigma_\mathrm{n} = \mathrm{Tr}\{\mathbf{Q}^1\mathbf{h}_\mathrm{n}^{01}\}$$

and extracting from the resulting formula the coefficient of the derivatives of the integral with indexes μ, ν, ρ, and σ yields

$$(\mu^*\nu|\rho^*\sigma)^1(2D_{\mu\nu}Q_{\rho\sigma} - D_{\nu\rho}Q_{\mu\sigma} + 2D_{\rho\sigma}Q_{\mu\nu} + D_{\mu\sigma}Q_{\nu\rho}) + \\ (\nu^*\mu|\rho^*\sigma)^1(2D_{\mu\nu}Q_{\rho\sigma} - D_{\mu\rho}Q_{\nu\sigma} - 2D_{\rho\sigma}Q_{\mu\nu} + D_{\nu\sigma}Q_{\mu\rho}) \qquad (11)$$

where the matrix $\mathbf{Q} = \mathbf{Q}^\mathrm{n}$ for the nth nucleus is defined as

$$\mathbf{Q}^\mathrm{n} = \textstyle\sum_{\mathrm{i,a}}(e_\mathrm{i} - e_\mathrm{a})^{-1} \times \mathbf{C}_\mathrm{i}^\dagger \mathbf{h}_\mathrm{n}^{01}\mathbf{C}_\mathrm{a} \times (\mathbf{C}_\mathrm{i}\mathbf{C}_\mathrm{a}^\dagger - \mathbf{C}_\mathrm{a}\mathbf{C}_\mathrm{i}^\dagger) \qquad (12)$$

We precalculate the maximum absolute value of each matrix element of $\mathbf{Q}$, $\mathbf{Q}_{\mu\nu}^{\max} = \max\mathbf{Q}_{\mu\nu}^\mathrm{n}$, where n runs over all nuclei for which the shielding is calculated. Using techniques similar to those of Schlegel[29] for gradient calculations, we can determine a nonstrict

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Table VI. Convergence of the Calculated NMR Shielding with the Basis Sets in the GIAO Method for Hydrogen Sulfide and Carbon Disulfide (ppm)[a]

Carbon Disulfide

basis set	^{13}C shielding iso	^{13}C shielding paral	^{13}C shielding perp	^{33}S shielding iso	^{33}S shielding paral	^{33}S shielding perp
6-31G	-56.46	291.64	-230.51	530.09	1062.73	263.77
6-31G (0,d)	-55.32	290.58	-228.28	560.70	1062.40	309.85
6-31G (d,0)	-36.89	290.14	-200.41	553.59	1062.28	299.05
6-31G (d,d)	-36.94	289.67	-200.25	575.45	1062.45	331.96
6-31G+(d,d)	-35.78	289.67	-198.50	578.35	1062.36	336.35
6-31G+(2d,d)	-32.93	289.85	-194.32	582.16	1062.49	342.00
6-311G	-53.62	291.61	-226.24	475.33	1062.56	181.71
6-311G (d,d)	-50.72	289.90	-221.05	551.19	1062.35	295.61
6-311G (2d,d)	-49.23	289.99	-218.93	560.78	1062.44	309.96
6-311G (3d,2d)	-51.45	289.90	-222.12	564.99	1062.43	316.26
6-2111G (3d,2p)	-53.30	289.82	-224.86	532.64	1062.41	267.76[b]
6-311G+(d,d)	-54.35	289.84	-226.45	551.52	1062.34	296.11
6-311G+(2d,d)	-51.69	289.92	-222.50	559.70	1062.39	308.36
6-311G+(2d,2d)	-52.49	289.89	-223.67	566.94	1062.38	319.21
6-311G+(3d,2d)	-52.44	289.86	-223.59	567.06	1062.38	319.40
6-2111G(3d,2d)	-53.30	289.82	-224.86	532.64	1062.41	267.76
6-2111G+(3d,2d)	-53.89	289.80	-225.74	534.20	1062.36	270.11
IGLO						
II	-45.7			516.0		
III	-56.1	287.0	-227.7	536.1	1047.4	280.5
IV	-57.1	287.1	-229.3	549.9	1068.3	290.8

Hydrogen Sulfide

basis set	^{1}H shielding iso	^{1}H shielding A	^{1}H shielding B	^{1}H shielding C	^{33}S shielding iso	^{33}S shielding A	^{33}S shielding B	^{33}S shielding C
6-311G	32.8	26.0	29.9	42.3	767.9	648.9	738.8	916.0
6-2111G[c]	32.8	26.0	29.9	42.3	745.1	614.2	713.0	908.3
6-2111G+	32.8	26.0	30.0	42.3	750.5	617.4	714.4	919.7
6-2111G+(2s)[d]	32.8	26.0	30.0	42.3	750.6	617.6	714.3	919.8
6-2111G+(d,p)	31.0	24.4	26.9	41.8	730.7	573.5	690.2	928.4
6-2111G+(3d,p)	30.9	24.5	26.8	41.6	713.2	542.8	670.6	926.2
6-2111G+(3d,2p)	30.8	24.3	26.6	41.5	715.7	546.1	672.6	928.3
6-2111G+(5d,3p)	30.8	24.3	26.5	41.5	712.6	541.7	668.7	927.2

[a] (nd,md) denotes *n* d orbitals on sulfur and *m* d orbitals on carbon IGLO results from ref 42; the basis sets II, III, and IV are all large; III is an S(12,8,3), C(11,7,2) basis, comparable to our best basis set. [b] This is a calculation with a decontracted 6-311G (3d,2d) basis, made to check the effect of contraction on the results. [c] The hydrogen s-type basis set was kept at the 6-311G level since preliminary calculations have shown that further increase in the flexibility of the s basis set on hydrogen had negligible effect. [d] Basis set augmented by two s-type functions on the sulfur atom.

upper limit for the contribution of a shell of integral derivatives to the NMR shieldings. This estimate includes the elements of $\mathbf{D}$ and $\mathbf{Q}^{max}$, as well as estimates for the integral derivatives. Examples for the efficiency of this scheme are given in section V. The only significant disadvantage of this procedure is that it requires the storage (or the recalculation) of the matrix elements of $\mathbf{h}_n^{01}$. For a large molecule with all shieldings calculated, this is a substantial amount of storage. If the integral magnitude estimation is not used, then an alternative program organization is preferable. In the latter, the first-order density in the external field is determined first, and the matrix elements of $\mathbf{h}_n^{01}$ are contracted with it as they are evaluated.

The above methods have been incorporated in our TEXAS ab initio program package.[30]

IV. Calculations

A large number of NMR chemical shielding calculations have been performed with the GIAO program; however, only a few will be discussed. The examples have been selected for the following reasons:

(1) To compare the accuracy and the efficiency of the GIAO implementation with other methods, with special focus on the individual tensor components, since there is less experience available with them than with the isotropic average.

(2) To examine the convergence of the calculated shielding constants with respect to the basis set quality. We are not aware of any systematic study of this extent. Establishing the convergence behavior is particularly important for second-row atoms, as the results for these appear to be more sensitive to basis set truncation than first-row atoms. For this reason, we have calculated ^{33}S chemical shifts for some representative sulfur compounds.

(3) To explore the limits of the GIAO chemical shift calculations by presenting timings for large molecules and systems with large basis sets.

Calculated shieldings are listed for the following molecules: methane, methyl fluoride, cyclopropane, cyclopropene, oxirane (ethylene oxide), and benzene, as well as the sulfur compounds hydrogen sulfide, carbon disulfide, the sulfate and thiosulfate ions, dimethyl sulfide, dimethyl sulfoxide, and dimethyl sulfone. Representative timings are given for some of these molecules, and also for some larger systems, like styrene, (*E*)-stilbene, the adamantyl cation, oxocane (C_7OH_{14}), octahydrocycloparaphane ($C_{16}H_{24}$), and the water cluster $(H_2O)_{17}$.

Unless noted otherwise, the calculations have been performed using the experimental geometries;[31] in most cases this means r_0 geometries when available. For the first-row elements Pople's basis sets 4-31G through 6-311G+(2d,2p)[32] have been employed. For sulfur the McLean–Chandler (12s,9p) basis set[33] was used, contracted to [6s5p], and augmented by one, two, or three sets of d functions (with exponents 0.515, or 0.2575 and 1.030, or 0.12875, 0.515, and 2.06) and by a set of diffuse s and p functions (exponents 0.05 and 0.03) has been used. Decontracting the 6-311G basis set further to 6-2111G had only a very small effect, less than 2 ppm in the absolute shieldings and much less in th relative shifts. However, the McLean–Chandler[32] basis set is apparently too strongly contracted in the 2p region, and decontraction to [6s,6p] (separating the exponents, which are 5.5045 and 2.2433 for sulfur) results in significant changes in the absolute shieldings and even in the shifts. Essentially all of this change is due to the paramagnetic

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Table VII. Convergence of the Calculated NMR Shielding with the Basis Set in the GIAO Method for the Sulfate and Thiosulfate Ions[a]

Sulfate

basis set	^{33}S iso	^{17}O iso	^{17}O aniso	energy, au
6-31G (d,d)	272.91	202.05	120.49	–696.779259
6-31G+(d,d)	249.21	185.95	123.37	–696.823301
6-311G (d,d)	262.76	182.16	125.48	–696.868280
6-311G (2d,d)	220.57	169.38	137.28	–696.905919
6-311G (3d,2d)	219.12	168.33	125.44	–696.948668
6-311G+(d,d)	246.72	167.65	125.38	–696.903067
6–311G+(2d,d)	210.37	159.63	132.89	–696.939406
6-311G+(3d,2d)	213.59	162.21	135.53	–696.976374
6–2111G+(3d,2d)	170.88	163.76	134.46	–696.978567

Thiosulfate

	^{33}S central		^{33}S thio		^{17}O	
basis set	iso	aniso	iso	aniso	iso	aniso
6-31G (d,d)	207.16	–35.82	573.10	626.66	133.32	149.58
6–31G+(d,d)	205.27	–49.34	524.27	723.94	118.81	150.22
6-311G (d,d)	224.35	–52.00	545.73	656.06	106.18	163.35
6-311G (2d,d)	181.08	–62.40	524.86	672.93	90.56	170.06
6-311G (3d,2d)	181.66	–66.76	513.39	701.54	90.58	163.78
6-311G+(d,d)	209.31	–39.66	496.51	742.23	96.68	160.00
6–311G+(2d,d)	173.39	–48.31	485.48	755.03	85.34	164.01
6–311G+(3d,2d)	173.58	–51.65	493.81	746.98	88.56	165.10
6–2111G+(3d,2d)	123.99	–53.14	466.09	782.57	89.64	164.05

[a] (nd,md) denotes *n* d orbitals on sulfur and *m* d orbitals on oxygen. The anisotropy is the difference of the parallel and perpendicular components of the shielding.

Table VIII. Isotropic NMR Chemical Shifts (ppm) in the Thiosulfate Ion Relative to the Sulfate Ion

method	^{33}S thio	^{33}S central	^{17}O
GIAO			
6-31G (d,d)	–300.19	65.75	68.73
6-31G+(d,d)	–275.06	43.94	67.14
6-311G (d,d)	–282.97	38.41	75.98
6–311G (2d,d)	–304.29	39.49	78.82
6-311G (3d,2d)	–294.27	37.46	77.75
6-311G+(d,d)	–249.79	37.41	70.97
6–311G+(2d,d)	–275.11	36.98	74.29
6-311G+(3d,2d)	–280.22	40.01	73.65
6-2111G+(3d,2d)	–295.21	47.89	74.12
exptl[a]		36.3	61

[a] Reference 45.

Table IX. ^{33}S Shifts in the Sulfate and Thiosulfate Ions Relative to Carbon Disulfide

		thiosulfate ion	
method	sulfate ion iso	central iso	thio iso
GIAO			
6-31G (d,d)	302.54	368.29	2.35
6-31G+(d,d)	329.14	373.08	54.08
6-311G (d,d)	288.43	326.84	5.46
6-311G (2d,d)	340.21	379.70	35.92
6-311G (3d,2d)	345.87	383.33	51.60
6-311G+(d,d)	304.80	342.21	55.01
6-311G+(2d,d)	349.33	386.31	74.22
6-311G+(3d,2d)	353.47	393.48	73.25
6-2111G+(3d,2d)	363.32	410.2	68.1
exptl			
(a)	350.3[a]	386.6[a]	
(b)	332[b]	368.3[b]	

[a] Calculated from data in ref 45. [b] Reference 46.

contribution. This is somewhat surprising in that the 2p function is expected to be largely atomic in nature and therefore should have no paramagnetic contribution. When comparing different calculations, we make use of the double-ζ or triple-ζ (DZ or TZ) and singly polarized (+P), doubly polarized (+2P) etc. notations. For instance, the 6-31G** basis in this notation is DZ + P. The addition of diffuse functions is denoted by a + sign, as usual.

In most cases, the calculated values are compared with both Hartree–Fock limit values (obtained by large basis sets) and with experimental chemical shifts. However, the Hartree–Fock limit values are more relevant in comparing different techniques for the following reasons. First, all methods considered here are based on the Hartree–Fock wave function, and therefore, any agreement better than the Hartree–Fock limit must be fortuitous. Second, comparison with experimental values suffers from uncertainties in molecular geometries, from condensed phase effects, and, in the case of the individual tensor components, from experimental difficulties in some instances.

Calculated NMR chemical shifts for two structures of the norbornadienyl cation and for norbornadiene, obtained with an earlier version of this program, have been published previously.[34]

V. Results and Discussion

Table I shows the convergence of the calculated shielding tensors with the basis set quality in methane and methyl fluoride. Convergence is essentially achieved at the triple-ζ plus polarization basis set level for ^{1}H, ^{13}C, and ^{19}F isotropic shieldings as well as for principal components of the carbon and fluorine shielding tensors in methyl fluoride. The influence of the diffuse orbitals is insignificant.

Recently, IGLO and LORG results were published for a series of fluoromethanes[35] with a focus on the influence of the basis set on the calculated shielding tensors. These results, and the CH_3F data from an extensive set of calculations on fluoro compounds by Fleischer and Schindler,[36] are compared with ours in Table II for CH_4 and CH_3F. In the case of the ^{13}C shielding the IGLO and GIAO results converge to essentially the same values; presumably, the LORG predictions would converge to a similar value with an analogous TZ + 2P basis set. However, the convergence of the GIAO results is much faster than both IGLO and LORG. Even with the small 4-31G basis, the GIAO results are satisfactory, and closer to the Hartree–Fock limit than the IGLO and LORG results with the DZ + P basis set. This faster convergence is particularly evident for the ^{19}F shielding tensor. For instance, the isotropic ^{19}F shielding varies for different basis sets by 92 and 51 ppm in the IGLO and LORG methods, respectively; with the GIAO method the maximum difference is only 6 ppm. The anisotropy of the ^{19}F shielding is even more striking. Without polarization functions, the IGLO and LORG values are of the wrong sign, while all of the GIAO values are in the correct range with correct signs, compared to both experiment[37] and the Hartree–Fock limit. However, the IGLO (and presumably the LORG) values improve very much when polarization functions are added.[36]

Table III shows the GIAO isotropic shieldings for the three-membered rings cyclopropene, cyclopropane, and ethylene oxide. Convergence is obtained at the TZ + P 6-311G(d,p) level for all nuclei. The principal components of the methylene ^{13}C chemical shift tensors (relative to methane; this is close to the generally used tetramethylsilane standard) are compared with IGLO, LORG, and experimental values in Table IV. (As the absolute shielding in methane is probably larger than in tetramethylsilane,[38] it is likely that the experimental values quoted should be increased by a few ppm. Following other workers in the field, we did not include this correction, as its magnitude is somewhat uncertain, and it is of the same order as condensed-phase effects, which preclude very accurate absolute comparisons of chemical shifts.) With large TZ + P basis sets the GIAO and LORG results agree

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Table X. Convergence of the Calculated NMR Shielding (ppm) with Respect to the Basis Sets in the GIAO Method. ^{33}S, ^{17}O, and ^{13}C Shieldings in Dimethyl Sulfide, Dimethyl Sulfoxide, and Dimethyl Sulfone[a]

	^{33}S		^{13}C		^{17}O	
basis set	iso	aniso	iso	aniso	iso	aniso
		Dimethyl Sulfide				
6-31G (d,0,0)	673.16	389.52	191.77	23.84		
6-31G (d,d,p)	686.08	281.58	184.99	25.40		
6-31G+(d,d,p)	680.09	273.53	183.93	27.14		
6-311G (d,d,p)	675.72	285.19	175.78	27.47		
6-311G (2d,d,p)	657.22	287.53	175.41	27.52		
6-311G+(d,d,p)	674.63	266.56	175.07	27.93		
6-311G+(2d,d,p)	654.23	279.33	175.02	27.72		
6-311G+(3d,2d,p)	650.52	285.62	173.77	26.95		
6-2111G+(3d,2d,p)	619.21	302.00	174.43	27.06		
		Dimethyl Sulfoxide				
6-31G (d,0,0)	327.13	335.00	173.10	51.09	328.74	242.69
6-31G (d,d,p)	345.41	324.23	167.83	49.73	341.28	229.53
6-31G+(d,d,p)	346.84	329.50	166.23	52.28	334.37	209.79
6-311G (d,d,p)	358.46	318.56	158.13	52.35	326.85	236.99
6-311G (2d,d,p)	315.98	356.81	157.48	52.32	312.84	240.23
6-311G+(d,d,p)	355.57	314.90	157.58	52.69	327.41	226.63
6-311G+(2d,d,p)	316.83	348.47	157.13	52.49	317.92	229.16
6-311G+(3d,2d,p)	299.48	354.92	155.61	51.60	315.60	224.51
6-2111G+(3d,2d,p)	250.88	376.38	156.08	51.88	317.46	226.92
IGLO II (2d,d,p)	273.5		147.4		318.0	
IGLO III	253.7	368.8	142.3	73.9	318.2	285.1
		Dimethyl Sulfone				
6-31G (d,0,0)	272.48	226.49	168.11	55.60	180.00	110.08
6-31G (d,d,p)	300.36	197.72	163.08	52.22	198.01	106.33
6-31G+(d,d,p)	299.26	192.14	161.68	52.94	193.28	108.93
6-311G (d,d,p)	313.40	205.15	152.96	54.99	174.89	115.71
6-311G (2d,d,p)	264.93	227.51	152.98	53.94	153.98	119.03
6-311G+(d,d,p)	307.77	203.58	152.44	55.30	177.21	115.29
6-311G+(2d,d,p)	265.87	219.00	152.70	54.17	161.70	122.50
6-311G+(3d,2d,p)	261.94	209.48	151.48	52.74	162.04	116.31
6-2111G+(3d,2d,p)	215.35	221.33	151.92	52.81	164.21	118.58

[a] The anisotropy is defined as A − (B + C)/2 where A, B, and C are absolute shieldings and A > B > C. IGLO results from ref 42. Basis set III used in the IGLO calculations is a very large uncontracted basis. The basis sets designated by the plus (+) sign (diffuse functions) contain diffuse functions only on the heavy atoms (S, C, O).

very well. Unfortunately, smaller (say DZ or DZ+P) LORG results are not available for these molecules; such results are a much more critical test of the method than large basis set results, and they are also more important for the projected routine applications for large systems. The IGLO results at the DZ level, particularly the individual tensor components, are in much poorer agreement with the large basis set values than the GIAO DZ (6-31G) data. Again, the addition of polarization functions improves the IGLO result very much,[41,42] although at considerable cost. We believe that our largest basis sets (TZ+P) approach the Hartree–Fock limit for these molecules. Agreement between the large basis (near-Hartree–Fock) and experimental tensor components[39] is only fair. It is not clear at this time whether the remaining discrepancy between theory and experiment is due to the neglect of electron correlation or is mainly experimental in its origin. For instance, the experimental assignment of the tensor components in ethylene oxide[39] was based on the DZ IGLO calculations,[40] which predict approximately equal BB and CC components. More accurate calculations, however, predict that the out-of-plane shielding is significantly smaller than the other components.

The GIAO results for benzene are shown in Table V. As before, convergence for the absolute shielding is reached at the TZ+P basis set level. However, for relative shifts reasonable values are obtained with the 6-31G basis set, as the errors cancel one another. The DZ IGLO and LORG chemical shifts are also in good agreement with experiment, presumably for the same reason. An interesting observation is that in all our results for first-row elements, the GIAO isotropic shielding decreases monotonically with increasing basis set quality. No such pattern is observed for IGLO or LORG (see, e.g., the ^{19}F results in Table II). This monotonic trend probably makes the GIAO chemical shifts more accurate than the IGLO or LORG ones. The final absolute shieldings are in excellent agreement with the gas-phase values of Jameson and Jameson.[38]

Relatively few accurate NMR chemical shift calculations have been published for second-row atoms beyond hydrides. Recent examples include the large-basis IGLO calculations by Schindler[42] and the GIAO calculations on ^{29}Si by Van Wazer at al.[43] To test the GIAO method with second-row nuclei, ^{33}S has been chosen as the representative nucleus. For ^{33}S, carbon disulfide is used as a common reference; theoretical calculations are sometimes referred to hydrogen sulfide. Our basis set tests for H_2S and CS_2 are presented in Table VI. For H_2S, decontracting the 2p region has a large effect on the ^{33}S chemical shift. Adding diffuse functions results in a change of ~5 ppm, while enlarging the McLean–Chandler basis further with s functions, or diffuse p functions, leads only to minor changes. Polarization functions are, as expected, important, and three sets of d functions are needed to obtain convergence to a few ppm. Similar results are

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Table XI. ^{33}S Isotropic Shifts (ppm) Relative to CS_2 in Dimethyl Sulfide, Dimethyl Sulfoxide, and Dimethyl Sulfone

method	MeSMe	MeSOMe	$MeSO_2Me$
GIAO			
6-31G (d,0,0)	−119.57	226.46	281.11
6-31G (d,d,p)	−119.63	230.04	275.09
6-31G+(d,d,p)	−101.74	231.51	279.09
6-311G (d,d,p)	−124.53	192.73	245.79
6-311G+(d,d,p)	−123.11	195.95	243.75
6-311G (2d,d,p)	−96.44	244.80	295.85
6-311G+(2d,d,p)	−94.53	242.87	301.07
6-311G+(3d,2d,p)	−83.46	267.58	305.12
6-2111G+(3d,2d,p)	−85.01	283.32	318.85
exptl		233 ± 20^a 312^b	315^c

[a] Reference 48. [b] Reference 49. [c] Annunziata, R.; Barbarrella, G. *Org. Magn. Reson.* **1984**, *22*, 250.

Table XII. ^{13}C NMR Shift Tensor Relative to CH_4 (ppm) in Dimethyl Sulfide and Dimethyl Sulfone[a]

			principal components		
method	iso	aniso	AA	BB	CC
	MeSMe				
IGLO (DZ)	12	34	31	15	−11
GIAO					
6-31G	16.71	27.71	30.90	20.99	−1.76
6-31G (d,d,p)	17.63	25.40	30.75	21.45	0.70
6-311G	20.62	28.89	35.59	24.34	1.36
6-311G (d,d,p)	21.31	27.47	35.71	25.23	3.00
6-311G+(d,d,p)	21.90	27.93	36.08	26.33	3.28
6-2111G+(3d,2d,p)	20.30	27.06	34.44	24.20	2.26
exptl	22	28	43	20	4
	$MeSO_2Me$				
IGLO (DZ)	41	85	77	66	−14
GIAO					
6-31G	42.91	67.49	72.21	58.59	−2.09
6-31G (d,d,p)	39.54	52.22	60.96	52.94	4.73
6-311G	46.88	65.29	75.10	62.15	3.33
6-311G (d,d,p)	44.13	54.99	66.54	58.39	7.47
6-311G+(d,d,p)	44.53	55.30	66.83	59.10	7.67
6-2111G+(3d,2d,p)	42.81	52.81	63.47	57.36	7.60
exptl	44	53	62	62	9

[a] IGLO and experimental results from Solun, M. S.; Facelli, J.; Michl, J.; Grant, D. M. *J. Am. Chem. Soc.* **1986**, *108*, 6464.

Table XIII. Effect of the Neglect of the Perturbed Two-Electron Integrals in Dimethyl Sulfone, with the 6-311G (d,p) Basis Set

threshold 10^{-n}	no. of 2e int.	time, s	^{33}S shielding, ppm
6	1 247 495	1598	359.49
7	1 494 012	1722	358.42
8	1 712 058	1835	358.46
9	1 902 199	1936	358.46
10	2 077 310	2027	358.46
15	2 750 960	2349	358.46

Table XIV. Timings for Large Basis Set NMR Chemical Shift Calculations on Dimethyl Sulfone, Benzene, and Phenylacetylene[a]

basis set	dimension[b]	energy time	shift time	ratio T_S/T_E
	$CH_3SO_2CH_3$ (C_s)			
6-311G	91	12.7	28.3	2.23
6-311G (d,d,p)	134	38.3	95.0	2.48
6-311G (2d,d,p)	139	44.0	108.9	2.48
6-311G+(d,d,p)	154	60.6	153.5	2.53
6-311G+(2d,d,p)	159	69.0	183.5	2.66
6-311G+(3d,2d,p)	184	117.7	308.5	2.62
	C_6H_6 (C_{2v})			
6-311G	96	7.5	14.1	1.89
6-311G (d,p)	144	22.9	51.8	2.27
6-311G+(d,p)	168	36.3	93.6	2.58
6-311G+(2d,2p)	216	89.7	225.1	2.51
GIAO (9s5p/4s2p)	72	5.5	12.4	2.26
IGLO (9s5p/4s2p)	72		total 20.0	
	Phenylacetylene (C_{2v})			
GIAO (9s5p2d/5s1p)	212	135.9	391.2	2.87
IGLO (9s5p2d/5s1p)	212	231	311	1.34

[a] Timings in minutes on the Apollo DN10000 workstation, for all nonequivalent nuclei. The symmetry group shown may be a subgroup of the molecular point group as TEXAS can use only idempotent symmetry operations (C_2, σ, i), and only those symmetry operations that transform different atoms into each other can be used efficiently. IGLO results from refs 35 and 51, scaled by factors of $1/40^{35}$ and 4^{51} to account for the speed of the computers used (see text).

obtained for CS_2. For this molecule the paramagnetic contribution to the parallel component of the shielding vanishes by symmetry. The remaining diamagnetic component, as a simple expectation value of r^{-1}, is insensitive to the basis set. The ^{13}C shielding is essentially converged with the 6-311G+(2d,d) basis set to −52.4 ppm, close to Schindler's estimate[42] of the Hartree–Fock limit. However, the sulfur shielding needs a 6-2111G+(3d,2d) basis set for convergence. Additional d functions, and also f functions on the sulfur (not shown in Table VI), cause little further change. It is somewhat disappointing that the final value for the ^{33}S isotropic shielding is still 47 ppm too low compared to the experimental absolute shielding, 581 ppm.[44] The theoretical absolute shielding for ^{13}C shift is also 46 ppm lower than the experimental gas-phase value,[38] −8 ppm. This appears to be a correlation effect, not surprizing in a molecule with low-lying π orbitals.

The thiosulfate ion is an interesting case. Only one ^{33}S resonance singal was observed, although the two sulfur atoms are chemically different.[45] The missing signal is the result of the fact that one of the sulfur nuclei has a resonance line too broad to be observed.[45] The observed ^{33}S signal was first assigned to the thio sulfur atom.[45] However, it was shown later that this signal belongs to the central sulfur atom.[46] This is also supported by ab initio electric field gradient calculations.[47] Our calculated results for the sulfate and thiosulfate ions are shown in Table VII. Even with the largest basis sets employed, convergence is not yet fully reached, although the final results for both ^{33}S and ^{17}O seem to be quite close to the convergence limit. The relative values shown in Table VIII agree very well with the experimental values. The signal of the central sulfur in $S_2O_3^{2-}$ is shifted downfield relative to SO_4^{2-} by 40 ppm (experiment, 36 ppm). The calculated downfield shift of ^{17}O nuclei, 74 ppm, agrees reasonably with the experimental 61 ppm.[46] The calculated ^{33}S chemical shifts relative to CS_2, shown in Table IX, agree well with experiment, in view of the difficulties of the latter. In these negative ions, diffuse s and p functions are, understandably, important. Their inclusion significantly decreases the calculated shieldings.

Calculated shieldings for a different class of sulfur-containing molecules, dimethyl sulfide, dimethyl sulfoxide, and dimethyl sulfone, are presented in Table X. As one would expect, convergence with the basis set is fastest for ^{13}C and the slowest for ^{33}S shieldings. Diffuse functions appear important only for ^{17}O shieldings, probably because of the partial negative charge on the oxygen atom. Table XI contains the calculated and experimental ^{33}S chemical shifts in these molecules, relative to CS_2. In the case of two contradicting experimental values for the sulfoxide,[48,49] the theoretical results are intermediate between the results of Retcofsky et al.[48] and Belton et al.[49] Table XII compares the calculated ^{13}C shifts (relative to methane) with IGLO and experimental results. For the sulfide and the sulfone, the agreement between the experimental results and the GIAO calculated values

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Table XV. Timings of the NMR Chemical Shielding Calculation for Larger Molecules[a]

molecule, formula, symmetry used[b]	geometry, total energy	basis set, dimension[c]	T_{int}	T_{SCF}	$T_{\text{shielding}}$
styrene, C_8H_8, C_1	4-21G adjusted,[d] −307.147 34	4-31G, 88	14.6	7.5	57.0
styrene, C_8H_8, C_1	4-21G adjusted,[d] −307.582 12	6-31G(d), 128	48.7	19.2	204.2
oxocane, $C_7H_{14}O$, C_s boat–chair 1	4-31G, −347.563 18	4-31G, 100	13.8	8.5	50.9
oxocane, $C_7H_{14}O$, C_1 boat–chair 3	4-31G, −347.563 85	4-31G, 100	26.8	13.3	97.6
adamantyl cation, $C_{10}H_{15}^+$ (C_s)	6-31G*,[e] −387.178 89	6-31G(d), 170	71.1	46.1	285.1
stilbene, $C_{14}H_{12}$, C_2 (trans)	4-21G adjusted,[d] −536.376 03	4-31G, 150	38.1	20.3	128.4
stilbene, $C_{14}H_{12}$, C_2 (trans)	4-21G adjusted,[d] −537.136 26	6-31G(d), 220	130.1	65.0	523.4
$C_{16}H_{24}$,[f] C_1	MMX, −618.896 78	4-31G, 192	233.3	174.2	1164.9
$(H_2O)_{17}$ C_s	X-ray diffr, −1290.638 21	4-31G, 221	288.4	94.0	859.4

[a] Times in CPU minutes on the Apollo DN10000 workstation, energies in atomic units. [b] The symmetry used is sometimes a subgroup of the full molecular point group; see the footnote in Table XIV. [c] Number of contracted basis functions. [d] Hargitai, R.; Szalay, P. G.; Fogarasi, G., to be published. For the adjustment, see: Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037. [e] Professor P. v. R. Schleyer, private communication. [f] *Ipso*-octahydroparacyclophane, geometry optimized by the MMX molecular mechanics method.

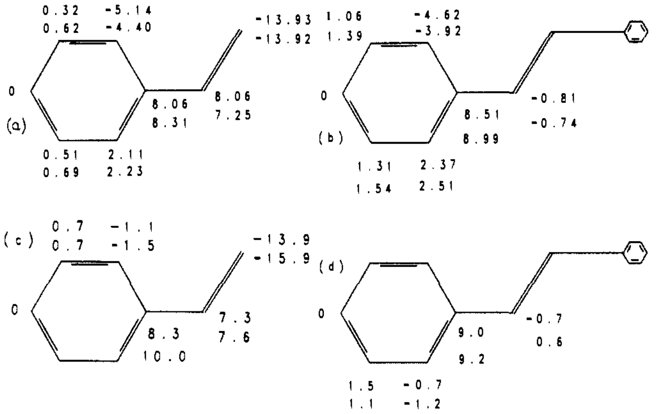

Figure 1. ^{13}C NMR chemical shifts in styrene and (*E*)-stilbene. All values in ppm relative to the para position; positive values correspond to a downfield shift. (a) and (b): calculated 4-31G (upper number) and 6-31G(d) (lower number) chemical shifts. (c) Comparison of the theoretical 6-31G(d) (upper number) and experimental (lower number) chemical shifts in styrene. Note the averaging of the ortho and meta positions, due to internal rotation. See: Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972; pp 71 and 197. A somewhat newer reference (Hamer, G. K.; Peat, I. R.; Reynolds, W. F. *Can. J. Chem.* **1973**, *51*, 897), on which most recent compilations are based, gives slightly different values for the α and β chemical shifts (+9.5 and −14.3 ppm, respectively). The overall agreement with the theoretical results remains about the same. (d) Comparison of the theoretical 6-31G(d) (upper number) and experimental (lower number) ^{13}C chemical shifts in (*E*)-stilbene. Note the averaging in the orth and meta positions, due to internal rotation. The experimental shifts were measured at −50 °C in chloroform-*d*. See: Meic, Z.; Vikic-Topic, D.; Gusten, H. *Org. Magn. Reson.* **1984**, *22*, 239. The chemical shift of the α-carbon relative to the para ring carbon changes decreases slightly with decreasing temperature, indicating that at least part of the observed sign discrepancy (−0.7 vs +0.6 ppm) is due to the effect of internal motion. See Table XV for the geometries.

is almost perfect for both isotropic shift and anisotropy. At the double-ζ level (6-31G in our calculations), the GIAO results generally agree better with experimental than the IGLO ones, in agreement with a trend noted earlier. The IGLO data in Table XII, particularly those on dimethyl sulfone, illustrate another point. It is possible to obtain fortuitously good agreement for the isotropic chemical shift and have significant errors in the individual tensor components.

We conclude this section with some timing results obtained on an Apollo DN10000 workstation. Table XIII illustrates our procedure of estimating and selectively neglecting two-electron integrals, described in section III. For a molecule of modest size, like dimethyl sufoxide, raising the threshold in the integral derivative evaluation from 10^{-15} to 10^{-7} produces a savings of almost a factor of 2 with little loss of accuracy. Although this is significant, more impressive savings have been reported for gradient[29] and SCF[50] calculations. The reason for this is not quite understood, and work is continuing on the integral neglect part of the program.

Table XIV contains timings for large basis set calculations on dimethyl sulfone, benzene, and phenylacetylene, while Table XV shows computer times for larger systems: the adamantyl cation, two conformers of oxocane, styrene, stilbene, an isomer of the strained molecule octahydroparacyclophane, and a microscopic ice cluster, $(H_2O)_{17}$. Table XIV also includes a comparison with IGLO timings[35,51] As the calculations were made on different computers, the comparison is approximate; we made the (conservative) assumption that the VAX 11/750 computer used in ref 35 is 40 times slower overall than our Apollo DN10000, and that the CYBER 205, with two vector pipes, is 4 times faster than the DN10000 for vectorized code. Based on the two comparisons (benzene with DZ basis, C_{2v} symmetry, and phenylacetylene with a 9s5p1d basis), our implementation of GIAO and the IGLO program of Kutzelnigg and Schindler shows comparable efficiencies. IGLO ought to be more efficient conceptually, and we surmise that the Gaussian lobe integral program compromises the efficiency of the IGLO implementation.[12]

The timings relative to the energy (integrals + SCF) calculations are also important, because they are less influenced by details of the coding. The results in Table XIV and XV show that GIAO chemical shielding calculations take, on the average, 2.5 times longer than the calculation of the energy. Therefore, if the energy calculation is feasible, then the NMR chemical shielding can also be calculated. Nevertheless, work is in progress to increase the efficiency of the chemical shielding program further. The shielding/energy timing ratio is close to 1 for IGLO,[51] suggesting that ultimately an IGLO calculation may be 1.8 times faster than a GIAO one. LORG, in its present implementation[13] includes an N^5 integral transformation step (in our opinion, this could be eliminated), and thus it is probably not competitive for large systems.

Our styrene and stilbene results are summarized in Figure 1. It is interesting to note that even minor differences in chemical shifts, like the 0.7 ppm difference between the para and meta carbon in styrene, are correctly reproduced by the calculations, as shown in Figure 1.

VI. Conclusions

The comparison of the GIAO and localized (IGLO[12] and LORG[13]) methods shows that the latter are more sensitive to the quality of the basis set employed. In other words, convergence of calculated chemical shieldings is faster with the GIAO method. In particular, calculations with double-ζ basis sets provide quite good results for organic molecules with the GIAO method. The localized method need polarization functions to achieve comparable accuracy. This is what one would expect, since the GIAO approach internally extends the basis set with higher angular momentum orbitals, which are necessary for the correct description of the perturbed system. In the localized methods, the flexibility of this extension is reduced, as all atomic orbitals participating in a localized molecular orbital share the same gauge factor,

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roughly the average of the atomic gauge factors. The greater flexibility of the GIAO wave function results in faster convergence. As the GIAO method can thus employ smaller basis sets, it may be ultimately the more efficient method, in spite of the savings offered by the localized techniques.

Another conclusion emerging from our calculations is that, unless large basis sets are used, the accuracy of individual tensor components is often lower with the localized methods than with the GIAO. This is true even in the cases where the isotropic average is correctly predicted by IGLO and LORG. By contrast, the tensor components are usually fairly well predicted by the GIAO method.

Finally, we would like to emphasize that our implementation of the GIAO method can be routinely used for NMR chemical shift calculations on fairly large molecules, say in the C_{10}–C_{15} range, on departmental workstations and minicomputers. Indeed, all results shown in this paper have been obtained on minicomputers. Our program currently runs on the IBM 4381 under CMS and VS1, on the IBM RT PC workstation under AIX, and on the Celerity 1200 and the Apollo DN10000 workstations under Unix. These versions, including integral, closed-shell SCF, and chemical shift calculations, are available for a nominal fee from the University of Arkansas. The whole TEXAS system, including many other features, some unique, such as a very compact integrals storage, UNO-CAS gradients, and a very efficient geometry optimization using automatically generated internal coordinates, will also be made generally available in the fall of 1990 from the University of Arkansas.

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Structure and Energetics of $C_2H_4Br^+$: Ethylenebromonium Ion vs Bromoethyl Cations

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Abstract: The cyclic and acyclic isomers of $C_2H_4Br^+$ are compared by using ab initio quantum mechanical techniques, including the use of electron correlation and polarization functions. The cyclic bromonium ion is found to be more stable than the acyclic 1-bromoethyl cation by 1.5 kcal/mol, in very good agreement with experiment. A transition state for the interconversion of these two forms is reported, the energy barrier being ~25 kcal/mol. The relative energies of the cyclic and acyclic minima are remarkably insensitive to basis set and electron correlation effects, validating the results of previous low-level studies. The 2-bromoethyl cation does not exist as a minimum on the potential energy surface and spontaneously collapses to the bromonium ion upon torsion.

Introduction

The addition of Br_2 to olefins is usually highly stereospecific, and the postulation in 1937 of a cyclic bromonium ion as an intermediate by Roberts and Kimball[1] was a radical suggestion. The detection of these intermediates was to come 30 years later in the pioneering NMR studies in superacid media from Olah's group.[2] In the interim, the mechanism for addition of Br_2 to double bonds via a bridged intermediate was widely accepted because it neatly accounted for why addition was anti: Br^+ is added to the double bond, forming a 3-membered ring, and attack by the remaining Br^- must come from the other side. The positive charge in the ethylenebromonium ion does not reside on the Br atom at all but primarily on the carbon atoms. Thus there is no attraction between the Br atom in the ring and Br^-, and steric factors are free to exert their full effect. A recent review by Ruasse[3] gives an account of the bromination of olefins, with consideration of whether bromonium ions or β-bromo carbocations are intermediates for various alkenes.

The open 2-bromoethyl cation is expected to be unfavorable because of the positive charge residing on a primary carbon: methyl substitution should stabilize this carbonium center relative to the bridged isomer. The positive charge on the carbon in the 1-bromoethyl cation is stabilized by Br, which is able to back-donate electron density. The global energy minimum should be either the open 1-halo form or the onium ion. The trend among halogens from experiment favors the open 1-halo isomer for F and Cl and bridging for Br and I.[4,5] There may not even be a cyclic ethylenefluoronium ion.

Ion cyclotron resonance experiments form Beauchamp's group[4] found two non-interconverting isomers of $C_2H_4Br^+$ and attributed the spectra to the 3-membered ring being 1.4 kcal/mol lower than the 1-bromoethyl cation which was made from a different source. This procedure has been criticized because the two different modes of product production may lead to differing levels of internal energy in the two isomers.[6] Because of its stereoselectivity, it has recently been reported that $C_2H_4Br^+$ has been used as a

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